X-Ray Absorption Spectroscopy and X-Ray Magnetic Circular Dichroism Studies of Transition-Metal-Codoped ZnO Nano-Particles

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We report on x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) studies of the paramagnetic (Mn,Co)-codoped ZnO [ZnO:(Mn,Co)] and ferromagnetic (Fe,Co)-codoped ZnO[ZnO:(Fe,Co)] nano-particles. Both the surface-sensitive total-electron-yield mode and the bulk-sensitive total-fluorescence-yield mode have been employed to extract the valence and spin states of the surface and inner core regions of the nano-particles. In the case of paramagnetic ZnO:(Mn,Co) nano-particles, the doped Mn and Co atoms are in a mixed-valence (2+, 3+, and 4+) state and the relative concentrations of the high-valence (3+ and 4+) Mn and Co ions are higher in the surface region than in the inner core region. In the case of the ferromagnetic ZnO:(Fe,Co) nano-particles, the doped Fe and Co atoms are found to be in a mixed-valence (2+ and 3+) state and the relative concentrations of the Fe3+ and Co3+ ions are higher in the surface region than in the inner core region. The XMCD spectra show that the Fe3+ ions in the surface region mainly give rise to the ferromagnetism while the doped Co ions in the surface region show only paramagnetic behaviors. The transition-metal atoms in the inner core region do not show magnetic signals, meaning that they are nonmagnetic states due to antiferromagnetic coupling. The present result combined with the previous results on transition-metal-doped ZnO nano-particles suggest that doped holes, probably due to Zn vacancy formation at the surfaces of the nano-particles, rather than doped electrons are involved in the occurrence of ferromagnetism in these systems. [DOI: 10.1380/ejssnt.2012.594]

Keywords: X-ray absorption spectroscopy; Nano-particles, quantum dots, and supra-molecules; Magnetic surfaces; Magnetic, structural, and other properties of nanostructures

I. INTRODUCTION

Various semiconducting oxides such as ZnO [1, 2], TiO2 [3, 4], and SnO2 [5, 6] in thin film and nano-particle forms are known to exhibit ferromagnetism at room temperature when they are doped with transition-metal atoms. Current interest in such magnetic nano-particle systems is motivated by unique electronic structures and magnetism at the surfaces of the nano-particles which are different from the inner core region. In the nano-particle form, the structural and electronic properties are modified by surface defects such as Zn and O vacancies with broken chemical bonds and charge imbalance, which may mediate or modify exchange coupling between the doped atoms [7]. For example, high-valence (3+ and 4+) Mn and Co ions are found to be present in the surface of paramagnetic (Mn,Co)-codoped ZnO nano-particles [8], probably due to the formation of Zn vacancies (VZn) in the surface region. In the case of Fe-doped ZnO system, the doped Fe atoms are converted from 2+ to 3+ due to hole doping in the surface regions [7, 9, 16], resulting in the ferromagnetic interaction between the doped Fe atoms. In the case of Co-doped ZnO systems such as (Co,Ga)-codoped ZnO [10] and Co-doped ZnO nanoparticles [11], on the other hand, oxygen vacancies (VO), which induce electron doping, are reported to be necessary for ferromagnetism. Recently, room-temperature ferromagnetism was reported for (Fe,Co)-codoped ZnO.
[ZnO:(Fe,Co)] nano-particle forms [12]. From the first-principle calculations, Karmkar et al. [12] have indicated that V\textsubscript{Zn}-mediated double exchange interaction plays important role for ferromagnetism in ZnO:(Fe,Co) nanoparticles. Indeed, enhancement of ferromagnetic interaction between transition-metal atoms has been demonstrated in previous first-principles calculations by Gopal and Spaldin [13]. First-principle calculations by Park and Min [14], on the other hand, have suggested the importance of RKKY-type exchange interaction mediated by conduction carriers induced by V\textsubscript{O} as the origin of ferromagnetism of ZnO:(Fe,Co). Also, calculations by Ghosh et al. [15] have indicated direct exchange interaction mediated by the doped electron carriers at the Fe-V\textsubscript{O}-Co defect configuration in the surface region of ZnO:(Fe,Co).

Thus, it has been controversial whether the magnetic interaction in the ZnO nano-particles comes from electron doping or hole doping. In this paper, we report on x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) studies of paramagnetic ZnO:(Mn,Co) and ferromagnetic ZnO:(Fe,Co) nanoparticles. The valence and spin states of the doped ions and their magnetic interaction have been revealed by XAS and XCMD measurements of the transition-metal core levels. Also, both the surface-sensitive total-electron-yield mode and the bulk-sensitive total-fluorescence-yield mode have been employed to extract the valence and spin states of the surface and inner core regions of the nano-particles separately. The experimental results indicate that doped holes rather than doped electrons are involved in the occurrence of ferromagnetism in these systems.

II. EXPERIMENTAL METHODS

Transition-metal-codoped ZnO nano-particles were synthesized by a low temperature chemical pyrophoric reaction process. We have prepared paramagnetic ZnO: (Mn,Co) nano-particles (Mn=15%, Co=15%), and ferromagnetic ZnO:(Fe,Co) nano-particles (Fe=5%, Co=5%) with T\textsubscript{C} > 300 K. Details of the sample preparation were described in refs.[12, 16, 17]. Structure characterization was carried out by x-ray diffraction (XRD), selected area electron diffraction (SAED) and transmission electron microscopy (TEM). We have made pellets from calcined powders and then sintered them at a temperature of ~570 K for 30 min. The average size of the nano-particles were 7-10 nm [12, 16].

XAS and XMCD measurements of ZnO:(Fe,Co) samples and XAS measurements of ZnO:(Mn,Co) samples were performed at the Dragon Beamline BL-11A of National Synchrotron Radiation Research Center (NSRRC), Taiwan. The spectra were taken both in the total-electron-yield (TEY: probing depth ~ 5 nm) and the total-fluorescence-yield (TFY: probing depth ~ 100 nm) modes, i.e., the TEY and TFY modes are relatively surface- and bulk-sensitive, respectively. The degree of circular polarization of x-rays was ~60%. XAS and XMCD measurements of ZnO:(Mn,Co) samples were also made at BL-16A of Photon Factory (KEK-PF). The degree of circular polarization of x-rays was more than ~90%. All the measurements were performed at room temperature.

Absorption spectra were analyzed using configuration-interaction (CI) cluster-model calculations. The cluster consisted of a transition-metal ion octahedrally and/or tetrahedrally coordinated by O\textsuperscript{2-} ions. The ground state wave function was expanded in the \psi = \alpha |d^\text{n}\rangle + \beta |d^{n+1}L\rangle + \gamma |d^{n+2}L^2\rangle, where \(\text{L}\) denotes an ligand O 2p hole. The adjustable parameters of the calculation were the charge-transfer energy \(\Delta\), the d–d Coulomb energy \(U\), the p–d transfer integral \(T\), and the crystal field splitting parameters \(\text{10Dq}\). We assumed high-spin states for the calculations, and \(\text{10Dq}\) was assumed to be less than 1.0 eV.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the Mn and Co 2p→3d XAS spectra (circles) of the paramagnetic ZnO:(Mn,Co) nano-particles, respectively, taken both in the TEY and TFY modes. Theoretical spectra (broken curves) of the Mn and Co ions in the 2+, 3+ and 4+ states calculated using the cluster model are shown.

![FIG. 1: Mn and Co 2p→3d XAS spectra (circles) of the paramagnetic ZnO:(Mn,Co) nano-particles, respectively, taken both in the TEY and TFY modes.](http://www.sssj.org/ejssnt)
in the TEY mode. We compare the Mn 2p→3d XAS spectra of the ZnO:(Mn,Co) nano-particles with those of Ca₁₋ₓMnₓRuO [18] and Zn₁₋ₓMnₓSe₂ [19], and compare the Co 2p→3d XAS spectra of the ZnO:(Mn,Co) nano-particles with that of Ti₁₋ₓCoxO₂[20]. It is likely that Mn 2p→3d XMCD spectrum comes from the Mn³⁺ and Mn⁴⁺ ions because the line shape of XMCD spectrum of ZnO:(Mn,Co) is similar to that of CMRO, where Mn³⁺ and Mn⁴⁺ ions coexist. The Co 2p→3d XMCD spectral line shape of the ZnO:(Mn,Co) nano-particles is similar to that of Ti₁₋ₓCoxO₂. From the experimental results, we suggest that paramagnetic component of the XMCD signals consists of the Mn³⁺, Mn⁴⁺ and Co²⁺ states.

Figures 3(a) and 3(b) show the Fe and Co 2p→3d XAS spectra of the ferromagnetic ZnO:(Fe,Co) nano-particles, respectively. In the figures, we compare the experimental spectra (circles) taken both in the TEY and TFY modes with the cluster-model calculations for the Fe and Co ions with various valence states, tetrahedrally or octahedrally co-ordinated by oxygen atoms [21]. In the transition-metal-doped ZnO nano-particles, the valence and the coordination of the doped atoms will be 2+(T₂) if no vacancies are created, or often become 3+(T₃) due to the vacancy formation in the surfaces [7, 9]. We therefore calculated spectra for the 2+(T₂), 3+(T₃), and 3+(O₈) states of the Fe and Co ions. Here, O₈ is an interstitial site of the Wurzite-type ZnO lattice. From the line-shape analysis shown in Fig. 3(a), one notices that the Fe ions in the surface region are mostly Fe²⁺(O₈) with a small amount of Fe³⁺(T₂). In the experimental XAS spectra taken in the TFY mode, the dip structure at 710 eV is shallower, that is, the Fe³⁺(T₂) component increases in the inner core region, suggesting that Fe³⁺(O₈) ions mainly come from the surfaces. From the Co 2p→3d XAS spectra, it is likely that the doped Co atoms in the surface region are Co²⁺(T₂), Co³⁺(T₃) and Co⁴⁺(O₈). On the other hand, the Co atoms in the inner core region appear to be largely in the Co²⁺(T₂) state.

Figures 4(a) and 4(b) show the Fe 2p→3d XAS and XMCD spectra of the ferromagnetic ZnO:(Fe,Co) nano-particles, respectively, taken at H=1 T. The Fe 2p→3d XMCD intensity taken in the TEY mode was finite, while the XMCD spectrum taken in the TFY mode showed...
Fe has a relatively large surface area, the spin-orbit coupling and magnetic anisotropy may be enhanced due to surface effects. Indeed, this large $M_{orb}$ has been observed for ZnO:Fe nano-particles [9]. Figure 4(c) shows the Fe 2p→3d XMCD spectra taken in the TEY mode at various magnetic fields. In Fig. 4(d), the XMCD intensities due to Fe$^{3+}(O_h)$ and Fe$^{2+}(T_d)$ are plotted as a function of magnetic field. The intensity due to Fe$^{3+}(O_h)$ increases with magnetic field but persists at low fields down to $H=0.2$ T, while the XMCD intensity due to Fe$^{2+}(T_d)$ remains unchanged with magnetic field. These results indicate that Fe$^{3+}(O_h)$ contributes to both the ferromagnetism and paramagnetism and that Fe$^{2+}(T_d)$ contributes only to the ferromagnetism.

Figures 5(a) and 5(b) show the Co 2p→3d XAS and XMCD spectra of the ferromagnetic ZnO:(Fe,Co) nano-particles, respectively, taken at $H=1$ T. The Co 2p→3d XMCD intensity taken in the TEY mode was finite, while the XMCD intensity taken in the TFY mode did not show finite intensity. This suggests that the Co ions in the surface region are magnetically active as in the case of Fe. One can see that the Co 2p→3d XMCD spectrum, taken in the TEY mode, comes from the Co$^{2+}(T_d)$ and Co$^{3+}(T_d)$ ions. Figures 5(c) and 5(d) show the Co 2p→3d XMCD spectra taken at various magnetic fields. The XMCD intensity increases with magnetic field, indicating that the ionic Co atoms in the surface region is paramagnetic and that the ferromagnetic component of the Co ions is negligibly small. The negligibly weak XMCD signals in the spectra recorded in the TFY mode indicate that the Co ions in the inner core region is magnetically inactive, that is, neither ferromagnetic nor paramagnetic, probably because they are antiferromagnetically coupled with each other. We thus conclude that the ferromagnetism of the ZnO:(Fe,Co) nano-particles comes only from the Fe ions in the surface region.

It should be noted that the Fe 2p→3d XMCD spectra of ZnO:(Fe,Co) indicate the spins of Fe$^{3+}(O_h)$ and Fe$^{2+}(T_d)$ signals to be in the same directions. Therefore the segregation of ferromagnetic or ferrimagnetic Fe oxides such as ZnFe$_2$O$_4$ [22, 23], γ-Fe$_2$O$_3$ [24], and FeO$_4$ [25] can be excluded because in these materials Fe$^{3+}(T_d)$ and Fe$^{2+}(O_h)$ are antiferromagnetically coupled [26]. Considering this and from the XRD, SAED and TEM results, we conclude that the ferromagnetism in these nano-particles are intrinsic and comes from the Fe$^{3+}$ and Fe$^{2+}$ ions in the surface region. A schematic picture of hole-mediated exchange interaction between Fe$^{3+}(O_h)$ and Fe$^{2+}(T_d)$ ions is shown in Fig. 6.

**IV. CONCLUSION**

In summary, we have investigated the electronic structure and magnetism of the paramagnetic (Mn,Co)-codoped ZnO and ferromagnetic (Fe,Co)-codoped ZnO nano-particles using 2p→3d XAS and XMCD. In the case of ZnO:(Mn,Co) nano-particles, the doped Mn and Co atoms are in a mixed-valence ($2^+, 3^+$, and $4^+$) state and the relative concentrations of the high-valence ($3^+$ and $4^+$) Mn and Co ions are higher in the surface region than in the deep core region. Mn and Co 2p→3d XMCD results suggest that the paramagnetism comes from the Co$^{2+}$,
Mn$^{3+}$ and Mn$^{4+}$ states. In the case of the ZnO:(Fe,Co) nano-particles, too, the doped Fe and Co atoms are found to be in a mixed-valence (2+ and 3+) state and the relative concentrations of the Fe$^{3+}$ and Co$^{3+}$ ions are higher in the surface region than in the inner core region. Fe and Co 2p→3d XMCD signals due to the ferromagnetic Fe ions and paramagnetic Fe and Co ions were observed in the surface region while no appreciable XMCD signals were observed in the inner core region. From these results, we conclude that the ferromagnetism of ZnO:(Fe,Co) nanoparticles comes from the hole-mediated exchange interaction between Fe$^{3+}$ and Fe$^{2+}$ in the surface region.

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